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Surface microstructural changes and release of ions from dental metal alloy removable prostheses in patients suffering from acid reflux

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Key words: metal alloy prosthesis, chromium, cobalt, molybdenum, nickel, leaching, surface microstructure, gastroesophageal reflux disorder

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Abstract

Purpose: Investigation of the surface microstructural changes and the release of ions from metal alloys used in removable dental prostheses and the potential effects of acidic reflux found in patients suffering from gastro-oesophageal reflux disease (GORD).

Materials and Methods: Thirty seven (37) patients were recruited. Data was gathered through a questionnaire and clinical examination. Samples of metal alloy from the dentures and patient's saliva were collected. GORD was confirmed using the GerdQ questionnaire. Denture samples were characterized using scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS), while salivary samples were tested for trace metal ions using inductively-coupled plasma (ICP).

Results: Characterization of denture samples revealed the presence of nickel, cobalt and chromium. Nickel-chromium exhibited an etched surface appearance, while cobalt-chromium exhibited no noticeable surface microstructural changes. Higher mean salivary levels of chromium and cobalt in patients wearing any metal alloy-based denture and of chromium and nickel in patients wearing Ni-Cr prosthesis were found to be significant. No differences were found in salivary metal ion levels of patients suffering from GORD.

Conclusions: Nickel-chromium alloy is prone to acid etching in the oral cavity while cobalt-chromium alloy appears to be more resistant. Cobalt, chromium and nickel are leached in saliva of patients making use of cast removable prostheses. The impact of gastric acid on metal ion release from dental metal alloys deserves further investigations.

Clinical significance: This preliminary study suggests that metal-based removable prosthesis leach trace metal ions in saliva. Nickel-chromium based dentures exhibit an etched appearance which is not related to GORD.

Introduction

Removable prostheses made of a base metal alloy have been used in dentistry since the 1930s.[1] The two main metal alloys used in their fabrication are the cobalt-chromium-molybdenum (Co-Cr-Mo) alloy and the nickel-chromium (Ni-Cr) alloy. A large variety of these alloys with different compositions are available on the market.[1]

In general both metal alloys have excellent mechanical properties with regards to strength, toughness and hardness,[2,3] along with adequate corrosion and wear resistance.[4] Alloys intended for intra-oral use should be resistant to corrosion[5] and chemical degradation.[6] Under normal conditions, alloys used in the oral cavity have been reported to leach heavy metals in the saliva. An *in vitro* study [5] indicated that metal ion leaching was pH dependant. Nickel and chromium leach out from metal alloys yet molybdenum and carbon were more stable.[5]

In patients suffering from gastro-oesophageal reflux disease, the oral conditions might be significantly worse because of the constant acid reflux. In fact the recognised main symptoms of GORD are frequent "heartburn" episodes and acid regurgitation which may or may not accompany the "heartburn" episode.[7] Other symptoms which are not always present can include epigastric pains, dyspepsia, dysphagia, nausea, odynophagia, vomiting and sleep disturbances.[7]

To date no clinical study has been carried out to measure the leaching of metal ions and their presence in saliva from patients wearing metal dentures. The aim of this study was to assess microstructural changes in the denture related to use and investigate the presence of heavy metal ions in the saliva of patients who wear metal alloy dentures. The relationship of these two phenomena with the occurrence of acid reflux in patients suffering from GORD was also investigated.

Materials and Methods

Patient recruitment

A cross-sectional study was used to assess the effect of acid reflux on metal ion leaching from intra-oral prostheses. Ethical approval for a clinical study was sought. Patients were recruited from the state hospital and also from gastrointestinal speciality clinics where the consultants have lists of patients suffering from GORD. A total number of 246 patients were identified as potential candidates for the study. Once the patients' charts were reviewed, a total number of 37 patients were recruited in the study.

One principal investigator interacted with participants. A questionnaire was given to all participants prior to a clinical examination. The questionnaire included questions on presence or absence of a denture and material of construction, the presence or absence of previous joint replacement surgeries (including the material used) and also the presence of oral or tongue piercings was noted. Patients were asked in detail about their acid reflux problems and if any problems were currently present.

A GerdQ questionnaire was also filled out. This was developed as a recent new tool for the diagnosis of GORD.[8] It consists of 6 questions with scores ranging from 0-3. The scores are cumulative (the maximum score achievable is 18. Patients scoring ≥8 are considered to suffer from GORD, while patients scoring <8 are not.[8] The results of this questionnaire helped categorize the 37 participants into patients who truly suffered from GORD and those who did not.

The patients who responded were divided into 4 groups as shown in Table 1.

Salivary sample collection and testing

A salivary sample was obtained after mouth rinsing. In addition, the patients were asked to avoid alcohol for 12 hours, dairy products for 20 minutes, food consumption within 60 minutes, tooth brushing within the 45 minutes, dental procedures within the 48 hours and drinking anything apart from water 60 minutes before sample collection,

The passive drooling method for saliva collection was used to collect samples. About 5 mL of saliva was collected. Any saliva samples that were visibly contaminated with blood or other constituents were discarded and the saliva collecting procedure was repeated. The salivary samples were placed in sterile, sealable containers.

Thirty-seven (37) saliva samples were tested. The saliva was pre-treated with a mineral acid in order to produce a low viscosity liquid. The samples were tested using specified analysis for chromium, cobalt, molybdenum and nickel with Inductively Coupled Plasma Emission Spectroscopy (ICP-ES).

Metal alloy sampling and characterization

Metal alloy samples from the dentures were obtained by sectioning any redundant part of the denture with a carborundum disc attached to a mandrel in a straight dental lab hand piece. The smallest possible sample size was obtained from each patient.

The denture samples were characterized by scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). The specimens were mounted on an aluminium stub, using carbon tape. Scanning electron micrographs at different magnifications in secondary electron mode were obtained. Energy dispersive spectroscopy (EDS) was performed at negative acceleration voltage of 15.00 kV and a working distance of 15 mm. Unused clasps made of Co-Cr and Ni-Cr alloys were also assessed.

Statistical analysis

All the data obtained was transferred to an SPSS statistical package for analysis. The Chi-Square test was used to assess pairwise associations between categorical variables. The Kolmogorov-Smirnov test was first used to assess normality for continuous variables. Where the variable followed a normal distribution, one-way ANOVA was used to compare mean variable values between the different groups. Where the data did not follow a normal distribution pattern, a non-parametric test, Kruskal-Wallis test was used to identify significant differences between mean values. The data obtained through ICP-ES analysis was compiled directly into an SPSS spreadsheet. The Kolmogorov-Smirnov test was used to assess normality. A non-parametric test, specifically the Kruskal-Wallis test was used to assess the significance of observed differences in Cr, Co, Mo and Ni mean values across the different levels of categorical variables.

Results

The response rate was 15% of 246 patients who had been identified. Fifty (50) % of individuals were not interested in participating in the study. The remainder wished to participate but were unable to, either due to health issues or due to logistical problems (like long working hours).

All the patients claimed that all their medical conditions were controlled and regulated with the appropriate medication. None of the study participants reported having had any oral or tongue piercings. Also all respondents answered that they had never undergone any joint replacement surgery.

Nineteen (19) participants made use of dental removable prostheses. Six (6) of these participants made use of acrylic dentures that had been in service for an average of 13 years ±9.0 with a range of 4-30 years. Thirteen (13) participants made use of a metal alloy-based denture. On average these dentures

had been in service for an average of 7 years ±1.95 with a range of 3-12 years. One of these dentures was a complete full upper denture, but the rest were partial dentures.

Denture sample assessment

The microstructure and elemental analysis of the two alloy types are shown in Figure 1 and 2. The new, unused samples (both cobalt-chromium and nickel-chromium) exhibited the same surface features, such as various scratches and indentations, which could be attributed to processing and forming of the metal. EDS analysis shows peaks for chromium, cobalt, molybdenum and silicon for the Co-Cr alloy (Figure 1) and nickel, chromium, molybdenum and aluminium for the Ni-Cr alloy (Figure 2).

The Co-Cr samples obtained from the patients' mouths (Figure 1) exhibited a smooth surface topography with some evidence of scratching produced by polishing similar to the unused alloy. The Ni-Cr sample exhibited an etched appearance which was evident throughout the material surface (Figure 2).

No noticeable differences were noted in the images between the alloys of the study group and those of the control group. The changes that were observed in the alloys of one group were observed equally in the other group.

Salivary sample assessment

The salivary assay results are presented in Table 2. Salivary metal ions were compared across different groups. Of the patients who possessed a metal denture (13), 3 of these were made of Ni-Cr, while 10 were Co-Cr based.

Salivary metal ions were first compared in patients with a metal denture and patients without a metal denture. Chromium and cobalt levels in the saliva of patients who possess a metal denture were significantly higher than in those patients who do not make use of a metal denture (chromium levels – X^2 (1) = 6.485, p = 0.011, cobalt levels - X^2 (1) = 4.285, p = 0.038, molybdenum levels - X^2 (1) = 0.942, p = 0.332, nickel levels - X^2 (1) = 0.881, p = 0.348).

The salivary metal ion levels were compared in patients wearing a Co-Cr based prosthesis and patients without a metal alloy prosthesis. Chromium and cobalt levels in the saliva of patients who possess a Co-Cr based denture were higher than in those patients who do not make use of a metal denture (chromium levels – X^2 (1) = 3.942, p = 0.047, cobalt levels - X^2 (1) = 6.237, p = 0.013, molybdenum levels - X^2 (1) = 1.202, p = 0.273, nickel levels - X^2 (1) = 0.003, p = 0.955).

Salivary metal ion level analysis in patients wearing a Ni-Cr based prosthesis and patients without a metal alloy prosthesis showed higher chromium and nickel levels in the saliva of patients who possess a Ni-Cr based denture (chromium levels – X^2 (1) = 4.510, p = 0.034, cobalt levels - X^2 (1) = 0.006, p = 0.938, molybdenum levels - X^2 (1) = 0.013, p = 0.908, nickel levels - X^2 (1) = 5.724, p = 0.017).

Furthermore, salivary metal ion levels were compared in patients suffering from GORD and those who did not. No significant difference in salivary metal ion levels was found between these two groups. (chromium levels – X^2 (1) = 2.259, p = 0.133, cobalt levels - X^2 (1) = 1.324, p = 0.250, molybdenum levels - X^2 (1) = 1.323, p = 0.250, nickel levels - X^2 (1) = 0.184, p = 0.668).

Salivary metal ion levels were finally compared in patients making use of a metal denture, between those patients suffering from GORD and those who did not. No significant difference was found in salivary metal ion levels between these two groups (chromium levels – X^2 (1) = 0.536, p = 0.464, cobalt levels - X^2 (1) = 0.771, p = 0.380, molybdenum levels - X^2 (1) = 0.774, p = 0.379, nickel levels - X^2 (1) = 1.371, p = 0.242).

Discussion

The case-control study investigated the impact of metal denture use and whether gastro-oesophageal reflux affected the metal used to construct the dentures. The GerdQ questionnaire is a validated questionnaire[8] and was therefore used in this study to confirm the presence or absence of GORD. Scanning electron microscopy enabled surface topographical imaging of the metal surfaces with no sample preparation. EDS analysis enabled the identification of elemental composition of the alloys.

The etched pattern visible in used nickel-chromium alloys is indicative of the cast microstructure with Ni-rich zones forming due to the preferential segregation of Ni-rich phase during solidification of the alloy.[9] These Ni-rich, Cr and Mo-depleted regions appear to suffer localised selective dissolution regardless of the presence or absence of acid reflux, resulting in high Ni ion concentration. Release of nickel is time dependant with high levels released initially which decrease over time.[10] Other metal alloys also showed this pattern of time-dependant release.[11, 12] Cobalt-chromium alloys, on the other hand, did not reveal any noticeable differences between the unused alloy and the used samples.

Patients who wore a Co-Cr based prosthesis, had significantly higher mean salivary ion levels for cobalt and chromium. Patients making use of Ni-Cr based prosthesis had significantly higher mean salivary ion levels for nickel and chromium. Molybdenum salivary ion levels were not significantly different. A recent study showed exacerbated release of metal ions from base-metal dental casting alloys treated with S. mutans, which was most likely result of the pH reduction during S. mutans growth. This exacerbated material cytotoxicity. The long-term stability of base-metal dental restorations in the oral cavity was considered to be a cause for concern,[13] thus in accordance to the findings in the current study.

GORD seemed to have little impact on salivary ion release in the study. GORD is not a static disease, and a single reading cannot be extrapolated to mean that what is happening at the moment of the reading,

is the actual scenario in the mouth all the time. Multiple, frequent readings over a period of time is needed to shed more light onto this. Furthermore, the numbers of patients eligible for participation in the study were quite limited. The recruitment of suitable candidates proved to be quite challenging, possibly limiting the validity of the findings. A larger sample size could have helped create a larger pool of suitable patients. In addition, any metal ions found in saliva are not necessarily being absorbed systematically. A better and stronger study would ideally involve blood sampling and ionic testing. Further investigations are necessary to study the interaction of metal alloys with biological tissues.

Conclusions

Within the limitations of the study, this research suggests that nickel-chromium alloy is susceptible to localised corrosion in the oral cavity while cobalt-chromium alloy appears to be more resistant. Cobalt, chromium and nickel are leached in saliva of patients wearing cast removable prostheses. The impact of gastric acid on metal ion release from dental metal alloys deserves further investigations.

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Table 1: Study group and control group details

		No. of candidates
Study Group	With metal denture/ symptomatic GORD	5
Control Group 1	With metal denture/ controlled GORD	8
Control Group 2	No metal denture/ symptomatic GORD	11
Control Group 3	No metal denture/ controlled GORD	13

Table 2 – Average salivary concentrations of Cr, Co, Mo and Ni between groups

		N	Mean ion leaching mg/L
Chromium	**Study Group**	5	0.112 ± 0.16
	Control Group 1	8	0.252 ± 0.41
	Control Group 2	11	0.057 ± 0.05
	Control Group 3	13	0.023 ± 0.01
Cobalt	**Study Group**	5	0.052 ± 0.03
	Control Group 1	8	0.541 ± 0.97
	Control Group 2	11	0.051 ± 0.05
	Control Group 3	13	0.021 ± 0.01
Molybdenum	**Study Group**	5	0.077 ± 0.07
	Control Group 1	8	0.093 ± 0.09
	Control Group 2	11	0.090 ± 0.10
	Control Group 3	13	0.042 ± 0.01
Nickel	**Study Group**	5	0.478 ± 0.91
	Control Group 1	8	0.410 ± 0.79
	Control Group 2	11	0.164 ± 0.21
	Control Group 3	13	0.081 ± 0.03

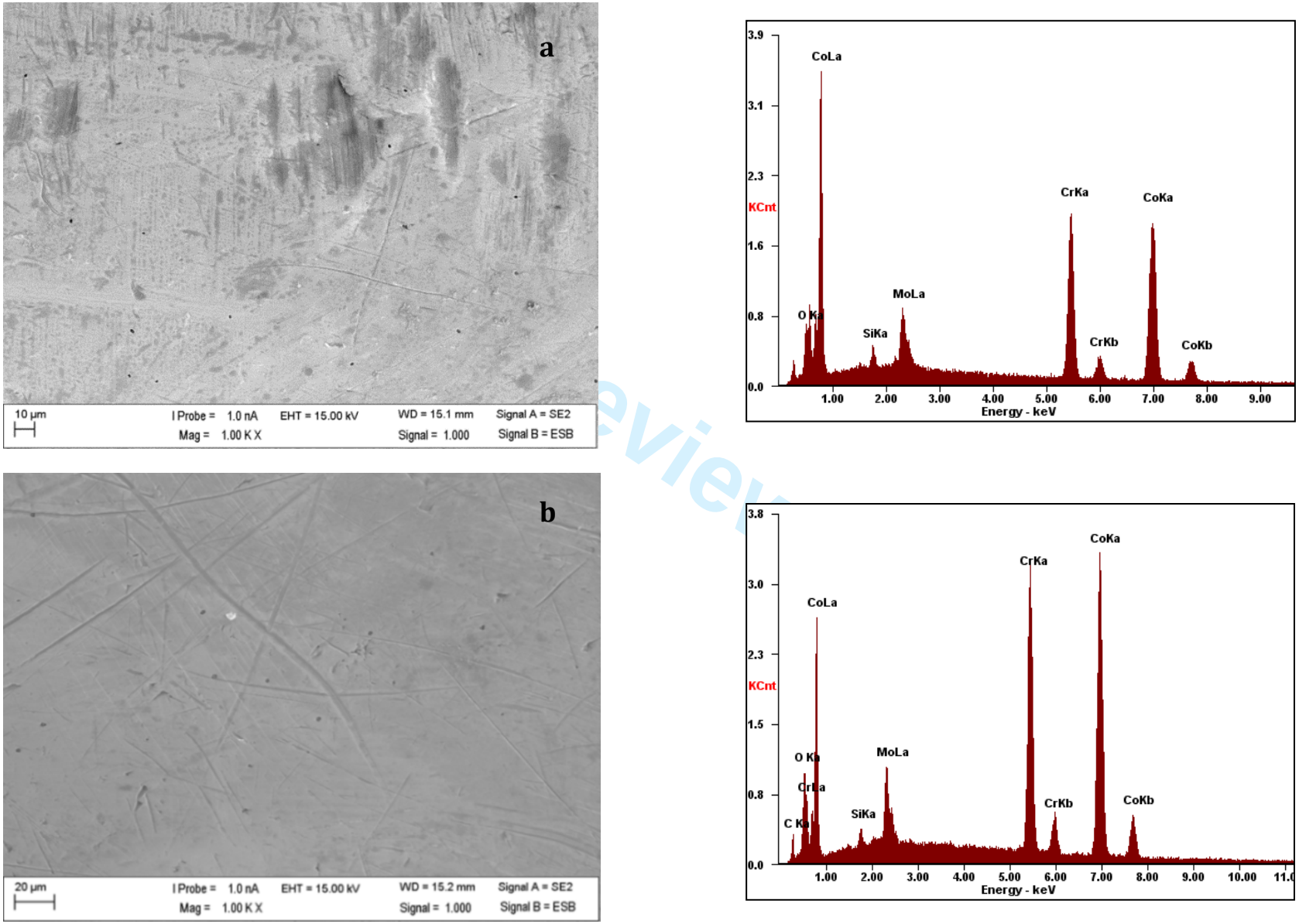

Figure 1- SEM image and EDS analysis of (a) unused Co-Cr alloy clasp and (b) used Co-Cr alloy clasp

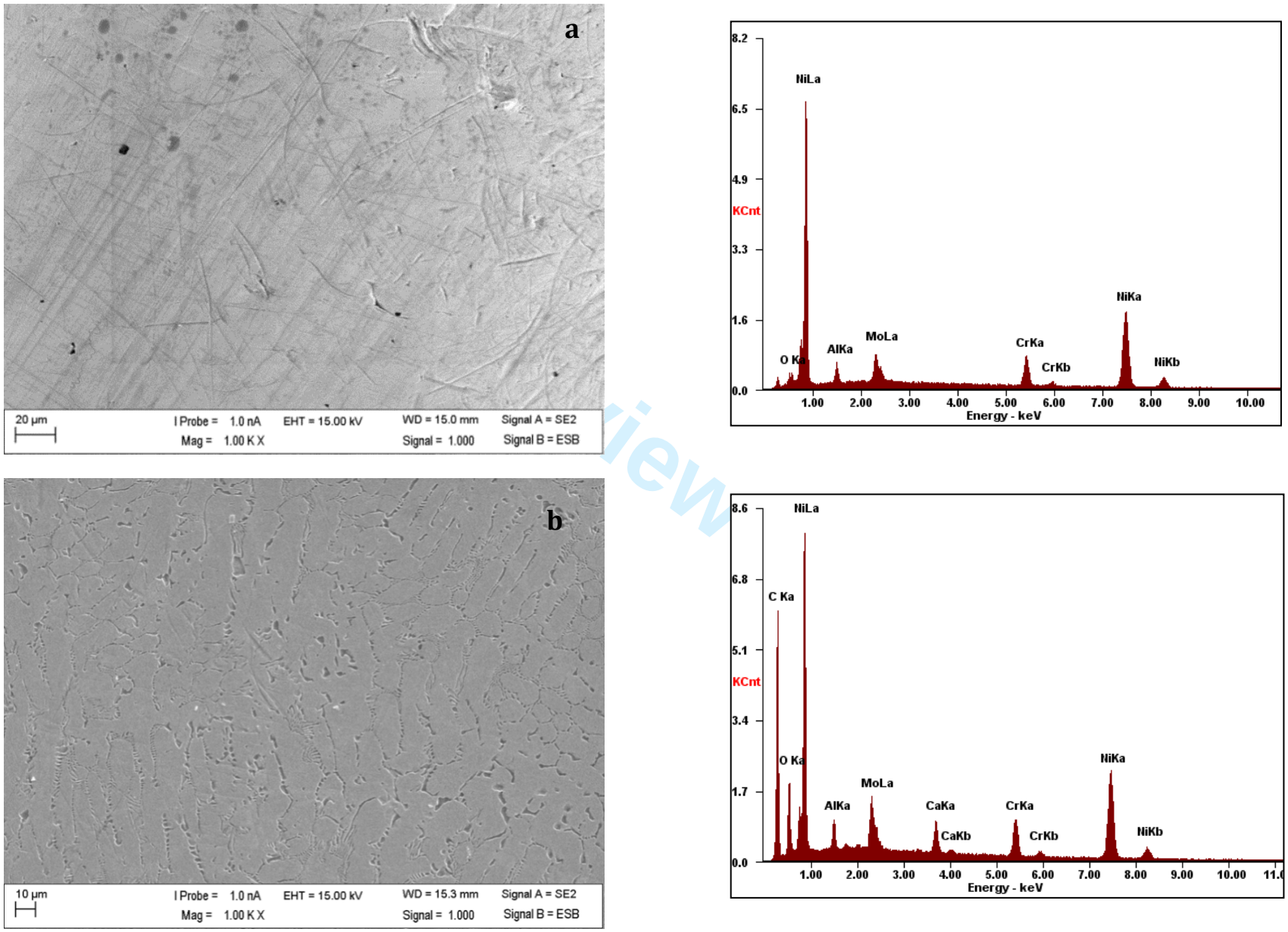

Figure 2 - SEM image and EDS analysis of (a) unused Ni-Cr alloy clasp and (b) used Ni-Cr alloy clasp